

CHEMCAM SULFUR QUANTITATIVE ANALYSIS AND INTERPRETATION. S.M. Clegg¹, R.B. Anderson², W. Rapin³, B.L. Ehlmann³, D.E. Anderson³, N.H. Thomas³, P. Gasda¹, J. Frydenvang⁴, O. Forni⁵, H. Newsom⁶, D. Blaney⁷, W. Goetz⁸, S. Maurice⁵, R.C. Wiens¹, ¹Los Alamos National Laboratory, Los Alamos, NM, sclegg@lanl.gov, ²USGS, Flagstaff, AZ, ³California Institute of Technology, Pasadena, CA, ⁴Univ. of Copenhagen, Copenhagen, Denmark, ⁵Institut de Recherches en Astrophysique et Planétologie, Toulouse, France, ⁶University of New Mexico, Albuquerque, NM, ⁷Jet Propulsion Laboratory, Pasadena, CA, ⁸Max-Planck-Institut für Sonnensystemforschung, Göttingen, Germany.

Introduction: The Curiosity rover has encountered many forms of sulfur including calcium sulfate veins [1], hydrated magnesium sulfates [2], and iron sulfates along the traverse through Gale crater. The chemistry and mineralogy of these sulfur-containing species have been primarily documented by the APXS and CheMin instruments [3]. An expanded SO₃ calibration model for the remote Laser-Induced Breakdown Spectroscopy (LIBS) technique used by the ChemCam instrument enables improved quantitative analysis of SO₃. Over the last year, SO₃ compositions have been reported with a new calibration model [4, 5]. This SO₃ calibration model has been expanded to include MgSO₄, Fe₂(SO₄)₃, and Na₂SO₄ [6]. In this paper, the details of this new LIBS calibration model will be described and applied to many disparate Mars targets.

The fundamental limitation with previous sulfur calibration models has been the relatively weak sulfur emission lines and the proximity of interfering iron emission lines. ChemCam LIBS major-element analyses are completed with a weighted ensemble of partial least squares (PLS) and independent components analysis (ICA) [7]. These multivariate techniques identify correlations between the concentrations of calibration samples and the pixel-by-pixel spectral variations. When these methods are used to quantify species with relatively weak emission lines such as sulfur, correlations with the larger major-element peaks tend to dominate the analysis.

This new sulfur calibration model is enabled by three improvements. First, the ChemCam LIBS spectrum is converted into a peak-area spectrum where each of the LIBS emission lines is integrated into a single peak converting the 6144 ChemCam spectral channels into typically fewer than 500 non-zero spectral points. Second, the PLS1 sub-model analysis developed by Anderson et al. is used segregate the sulfur calibration into three geologically relevant models [8, 9]. The sulfur model used to analyze samples on Mars is the integration of the PLS1 sub-model technique using the peak-area calibration spectra as shown in Figure 1.

Laboratory Calibration: The ChemCam instrument completed a re-calibration that is based on a significantly expanded set of standards. The original ChemCam calibration included 66 geochemical stand-

ards analyzed with the flight model prior to rover integration [10]. The ChemCam testbed at Los Alamos National Laboratory was used to collect the new LIBS geochemical database that includes more than 500 geochemical standards that are representative of the samples observed in Gale crater [7]. The sulfur composition of these rock powder standards alone was not diverse enough to represent the range of samples probed by ChemCam in Gale crater, so a series of doped samples containing various mixtures of CaSO₄, MgSO₄, Fe₂(SO₄)₃, and Na₂SO₄ [6] in either BHVO2 or K1919 [4-6] are included in the latest model. All of these spectra were processed as described by Wiens et al. [10].

Peak-Area Multivariate Analysis: All of the calibration spectra used in the new geochemical database were converted into peak-area LIBS spectra. Each

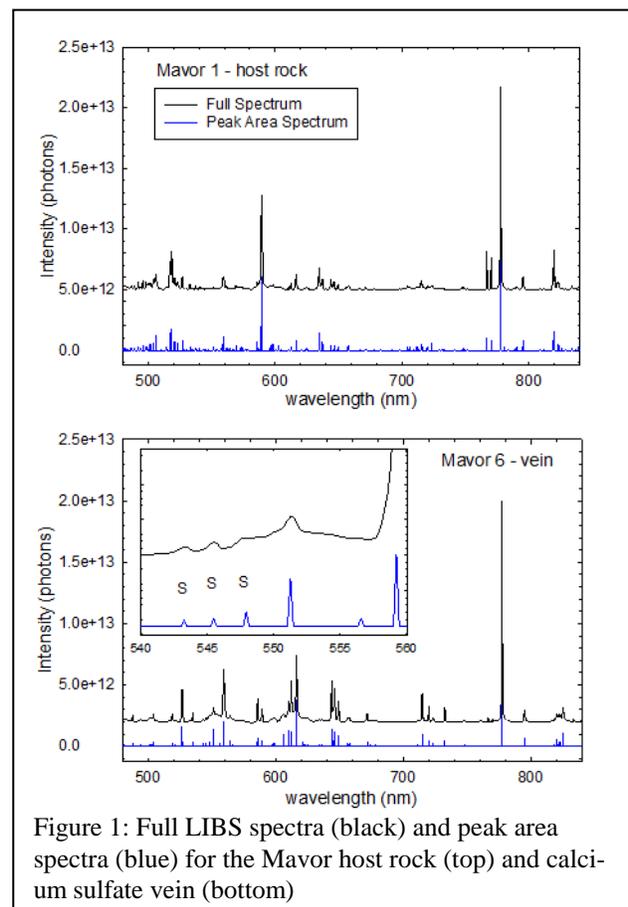
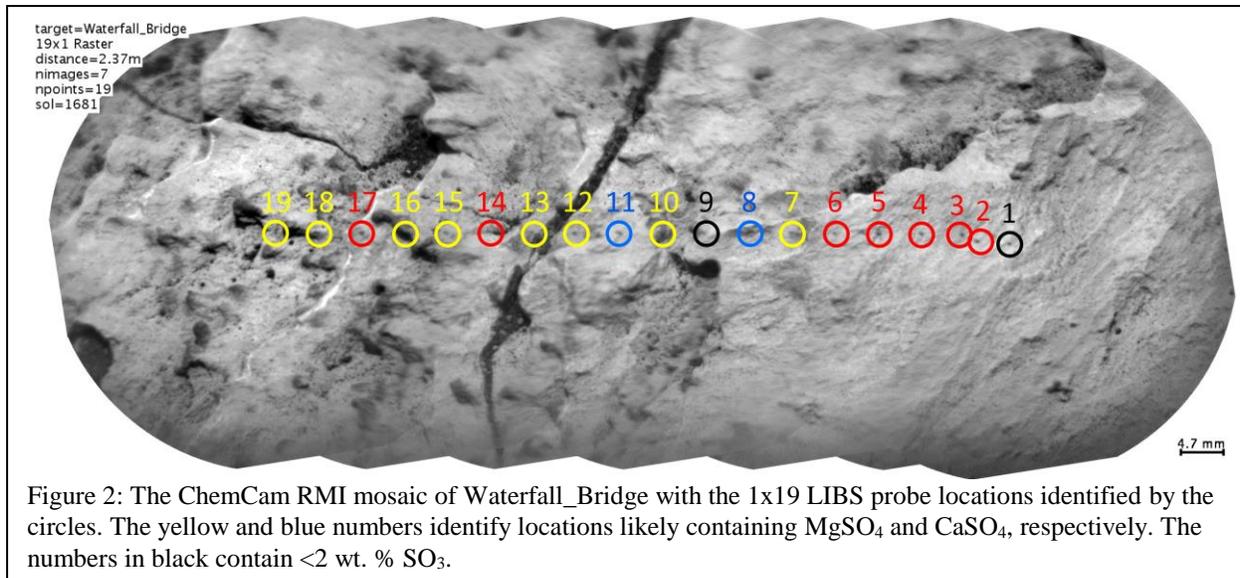


Figure 1: Full LIBS spectra (black) and peak area spectra (blue) for the Mavor host rock (top) and calcium sulfate vein (bottom)



spectral peak, independent of the identity of the elements responsible for the peak, was integrated into a single spectral feature.

These peak-area spectra were used to generate three overlapping PLS1 sub-models. Pure calcium sulfate veins would contain between 46.5 and 58.8 wt. % SO_3 for gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and anhydrite (CaSO_4), respectively. MgSO_4 , $\text{Fe}_2(\text{SO}_4)_3$, and Na_2SO_4 are likely to contain as much as 58, 60, and 56 wt. % SO_3 , respectively. Consequently, the “high” SO_3 model covers 30 – 100 wt. %. The “low” model covers 0 – 20 wt. % and represents most of the rocks and soils probed by ChemCam. The “medium” model covers the compositions between these two extremes, 15 – 35 wt. %, and could represent various sulfate structures such as calcium sulfate cemented sandstones. Finally, seamless transitions between these three overlapping models were defined as described by Anderson et al. [9]. Specifically, the low-to-medium transition covered the 15 – 20 SO_3 wt. % and the medium-to-high transition covers the 30 – 35 SO_3 wt. %.

Discussion: The focus of this effort has been on the development of a LIBS calibration model designed to extract SO_3 compositions from increasingly diverse chemical matrices. Waterfall_Bridge is an example of a chemically complex ChemCam target and the LIBS spectra document the chemical heterogeneity of the 19 locations probed.

Figure 2 contains the ChemCam RMI mosaic of the Waterfall_Bridge target and the colors of the numbers highlight the SO_3 chemical diversity. The eight locations identified by yellow numbers represent locations with elevated MgO ranging from 10.0 – 16.0 wt. % and <1.8 wt. % CaO. The corresponding SO_3 concentrations range from 5.4 – 15.4 wt. % and suggests that

these locations contain some MgSO_4 . In contrast, the two locations identified by blue numbers contain elevated CaO ranging from 18.7 – 19.2 wt. %. This new SO_3 calibration model indicates that these two locations contain 12.5 and 15.3 wt. % SO_3 , respectively. Finally, the SO_3 model also indicates that locations 1 and 9, highlighted by black numbers, contain <2 wt. % SO_3 .

Conclusions: Several improvements have been made to enable the quantitative analysis of SO_3 in ChemCam data. First, the ChemCam testbeds at Los Alamos National Laboratory and at L’Institut de Recherche en Astrophysique et Planétologie (IRAP) enable the ChemCam team to expand our geochemical library to quantify the sulfates discussed here. The development of the PLS1 sub-models approach allows one to further customize the model and account for the various matrices observed with ChemCam on Mars [7–9].

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